Semipermeable Membrane From Ionomeric Self-Assembling Block Copolymer

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Abstract

Morphological studies have been performed on novel polystyrene-polyisobutylene-polystyrene (PS-PIB-PS) triblock copolymer films made by different processes. The PS-PIB-PS films are composed of approximately 30% polystyrene end blocks. Small-angle x-ray scattering (SAXS) and transmission electron microscopy (TEM) confirm that a self-assembled, segregated cylindrical morphology forms in the copolymer. Dynamic mechanical analysis (DMA) is used as a tool to investigate the structure-property relationships in these polymers. Fourier-transform infrared (FTIR) spectroscopy and solvent-sorption studies have validated the membrane transport properties. Modified PS-PIB-PS copolymers have also been characterized. Modifications of the copolymers were carried out by converting approximately 20% of the polystyrene end blocks to styrene-sulfonic acid. The presence of sulfonic acid groups disrupts the morphology and significantly enhances water transport properties. Morphological features of the copolymers are discussed as they relate to mechanical and transport properties.

Table of Contents

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List of Figures

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List of Tables

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1. Introduction

The U.S. Army requires that all fielded systems be survivable in a chemical-warfare environment. Butyl rubber is currently used in standard protective clothing because it provides good protection from chemical and biological agents. However, garments made from butyl rubber are bulky and nearly impermeable to air and moisture, resulting in unbearable levels of heat inside the garments during use. One challenge at the U.S. Army Research Laboratory (ARL) is to develop and characterize advanced polymeric materials for soldier protective clothing that can block entry of harmful chemicals and simultaneously allow transport of water vapor from the soldier. To address this problem, research has been directed toward developing a flexible, triblock copolymer with "membrane-like" characteristics, formed via molecular self-assembly.

Self-assembled morphologies occur in block copolymers that are composed of thermodynamically immiscible constituent blocks. Ordered microstructures including spheres, cylinders, or lamellae can be observed, depending on the chemical composition of the blocks, sample preparation, interactions between the blocks, or by the addition of diluent [1]. Block copolymers in which an amorphous block is present as a major constituent and a glassy block exists as a minor component typically exhibit the solid-state properties of thermoplastic elastomers. When a portion of the polymer chain contains an ionic group, the block copolymer is classified as an ionomer. Association of ion-rich domains occurs in ionomers, providing "physical" cross-links that affect the block copolymer morphplogy and the thermal and mechanical properties [2]. This paper addresses the structure/property relationships observed in a polystyrene-polyisobutylene-polystyrene (PS-PIB-PS) block copolymer as a result of ionomeric modification in the PS end blocks.

A commercially available triblock copolymer formulation consisting of a PS-PIB-PS backbone was studied. The polymer comprised approximately 30% (molar) polystyrene. The thermoplastic elastomers exhibit physical properties of rubber at low temperature and melt-processable thermoplastic at temperatures above the glass transition temperature (T_g) of PS.

1

This behavior results from microphase separation of the glassy PS domains that act as physical cross-links dispersed in the rubbery PIB matrix. The fraction of PS controls the morphology that is formed in the copolymer (cylinders, lamellae, or spheres). Cylindrical morphology exists in the PS-PIB-PS triblock composed of 30% PS. Thus, the morphology formed by the PS fraction provides a "channel" by which molecular transport across the film can occur while the PIB matrix provides chemical resistance. Ionomeric modification of commercially available PS-PIB-PS copolymer was performed by sulfonation. Approximately 20% of the styrene monomers were converted to styrene-sulfonic acid. The modified copolymer exhibits hydrophilic character that is necessary for transporting water vapor. The polymers were characterized in their unmodified and sulfonated form utilizing a number of experimental techniques including dynamic mechanical analysis (DMA), transmission electron microscopy (TEM), small-angle x-ray scattering (SAXS), solvent-sorption experiments, and Fourier-transform infrared (FTIR) spectroscopy transport experiments.

2. Experimental

Kuraray, Inc. supplied the PS-PIB-PS triblock copolymers. The copolymers were sulfonated in a solution of dichloroethane and hexane at 50 °C with acetyl sulfate. Details of the sulfonation procedure are found elsewhere [3]. The copolymers were dissolved in toluene or toluene/hexyl alcohol mixtures at a concentration of 1% and were cast into Teflon petri dishes. Samples were identified by the rate of solvent evaporation and designated as "fast," "intermediate," or "slow." An "ultrafast" evaporation rate was achieved by spraying a solution (5% polymer concentration) onto a substrate and allowing the film to form under a hood.

DMA was performed using an Imass, Inc. autovibron (automated Rheo-200 rheovibron, Toyo Instruments). Films of approximately 0.01-cm thickness were evaluated between −130 °C and +100 °C at a heating rate of 1 °C per minute. Data were collected at 1 Hz. Solvent-absorption data were collected by submerging dry samples in high-performance liquid chromatograph (HPLC)-grade water for specific time intervals. Weight measurements were taken until saturation was reached. Weight averages were used to calculate solubility (S) defined

as weight of liquid absorbed per weight of dry sample. Water-diffusion experiments were performed using a HP5890 gas chromatograph (GC). A cylindrical fixture held the sample membrane horizontally, while the top surface of the sample was flooded with HPLC-grade water. The other side of the sample was swept with dry nitrogen and sent to a split injector of the GC oven equipped with a thermal conductivity detector (TCD).

Transport properties of the sulfonated block copolymer membranes were investigated using a Nicolet Research Series FTIR spectrometer with a horizontal attenuated total reflectance (ATR) cell and a zinc selenide trapezoidal ATR crystal. The polymer-coated ATR crystal was mounted in a flow-through ATR cell. Liquid penetrants are allowed to pass through the cell, flooding the polymer-coated ATR crystal. Diffusion of the penetrant through the polymer film is detected by the infrared (IR) absorbance. Details regarding the experimental apparatus and methodology used for the diffusion experiments are discussed elsewhere [4, 5].

TEM characterization was performed on cast samples coated with a 100-nm gold layer. A JEOL 100CX TEM microscope operated at 100-kV accelerating voltage was utilized. TEM samples were prepared by cutting 30- to 80-nm-thick sections using a cryomicrotome, and staining in RuO_4 vapors for 4 hr.

SAXS was performed on beamline X27C at National Synchrotron Light Source, Brookhaven National Laboratory. Data were collected using a pinhole collimated beam and image plate detectors and were reduced by background subtraction and circular averaging. The wavelength used was 1.54 Å. The sample to detector distance was about 1,000 mm.

3. Results and Discussion

3.1 DMA. The tensile storage modulus E', loss modulus E", and tan δ are plotted as a function of temperature and shown in Figure 1. E' shows a distinct drop at the (T_g) of the PIB matrix and another decrease that begins at approximately 93 °C associated with onset of the glass
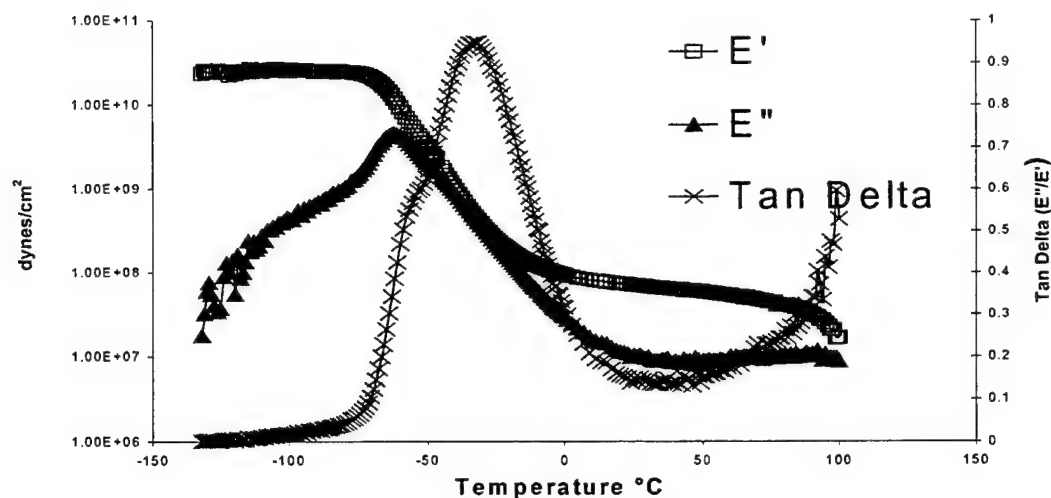
3

Figure 1. DMA of Unmodified PS-PIB-PS Copolymer.

transition of the PS domains. The tan δ curve exhibits a low-temperature shoulder at approximately −60 °C that is likely a contribution from less-restricted PIB chains. The T_g of pure PIB is −70 °C [6]. The low-temperature shoulder appears to correspond with the peak of E". The T_g is defined as the temperature corresponding with the maxima in the E" data and was measured at approximately −63 °C for the PS-PIB-PS copolymers. T_g was previously reported for noncommercial PS-PIB-PS polymers to be approximately −65 °C using differential scanning calorimetry DSC [7], which is in good agreement with the DMA data.

Variation in the solvent evaporation rate did not have a significant effect on dynamic mechanical behavior. The most apparent difference was observed between films formed via the fastest evaporation rate (spraying) and the slowest evaporation (2 or 3 weeks required for film formation). Films formed via slow evaporation exhibited slightly higher values of E' and slightly higher magnitudes of E" and tan δcompared to the sprayed films. These data are shown in Figures 2, 3, and 4, respectively. TEM confirmed that slow solvent evaporation rates during film formation resulted in better long-range order compared to fast evaporation rates. Cylinders formed by the glassy styrenic blocks were oriented with their axes parallel to the film plane. This morphology is consistent with the E' shown in Figure 2. An increase in the tensile storage
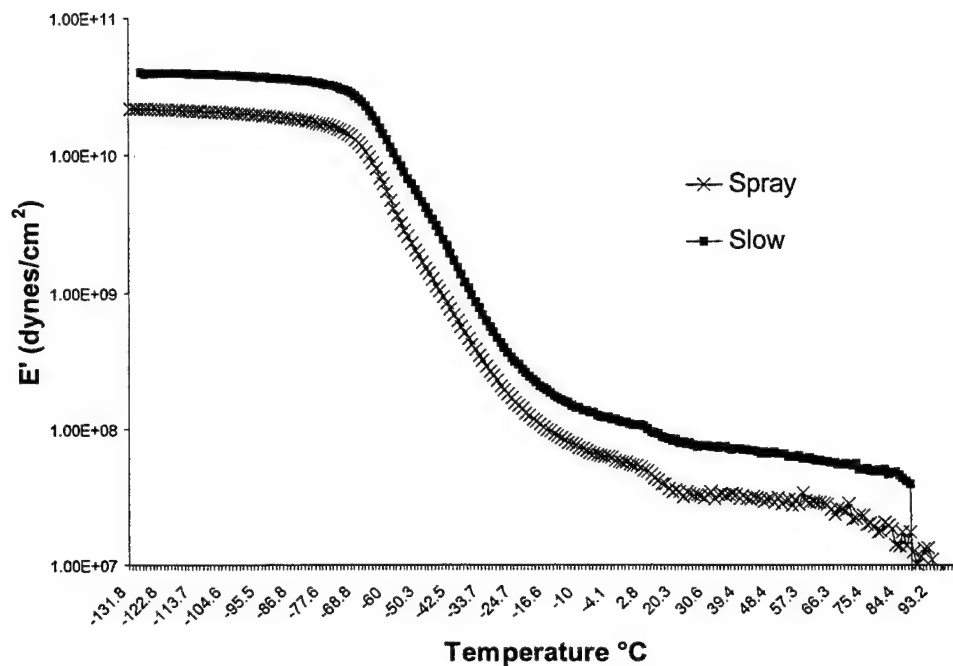
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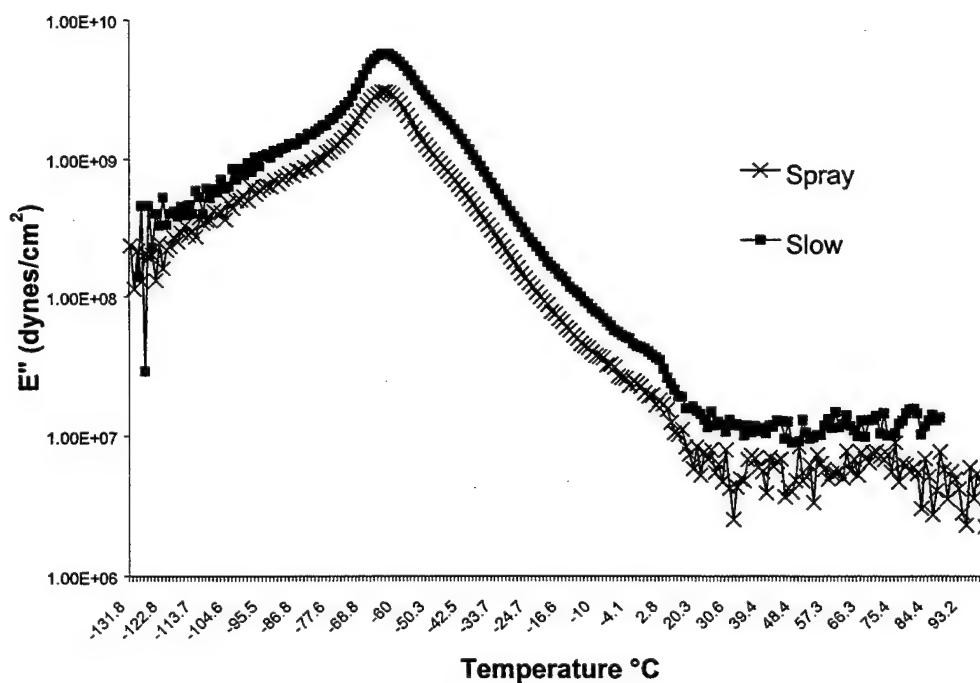**Figure 2. E' of PS-PIB-PS Films Formed by Different Processing Methods.**

Figure 3. E" of PS-PIB-PS Films Formed by Different Processing Methods.
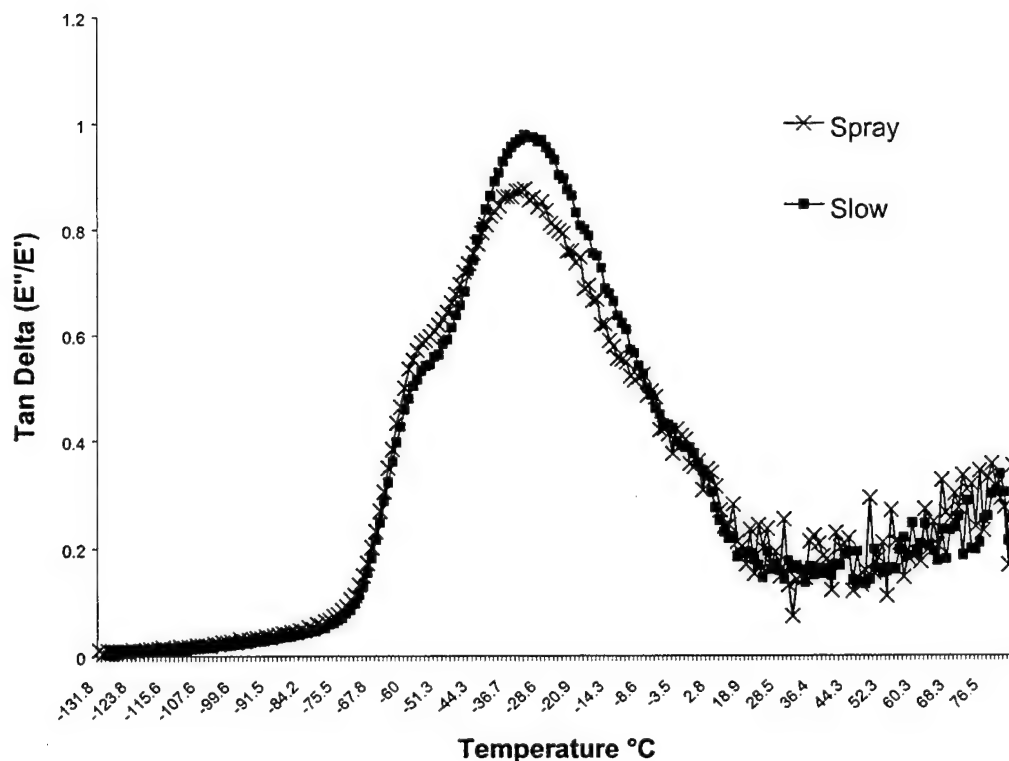
5

Figure 4. Tan δ of PS-PIB-PS Films Formed by Different Processing Methods.

modulus would be expected when the glassy cylinders exist parallel to the film plane. The changes in loss properties shown in Figures 3 and 4 suggest that a more disordered morphology caused by "ultrafast" evaporation rates (spraying) may inhibit the microphase separation of the PS and PIB domains causing a slight reduction in E" and tan δ peak magnitude. This result was observed to a much greater extent following sulfonation. Kim and Libera [8, 9] previously reported on the effect of solvent evaporation rate on thin film morphology of similar triblock copolymers.

Sulfonation of the PS-PIB-PS copolymer had the greatest effect on dynamic mechanical behavior. DMA results for PS-PIB-PS copolymers and their ionomers are shown in Figures 5–7. Figure 5 shows E' plotted as a function of temperature for the two polymers. Sulfonation of the block copolymer resulted in a much higher rubbery E'. The ionomer was observed to be more
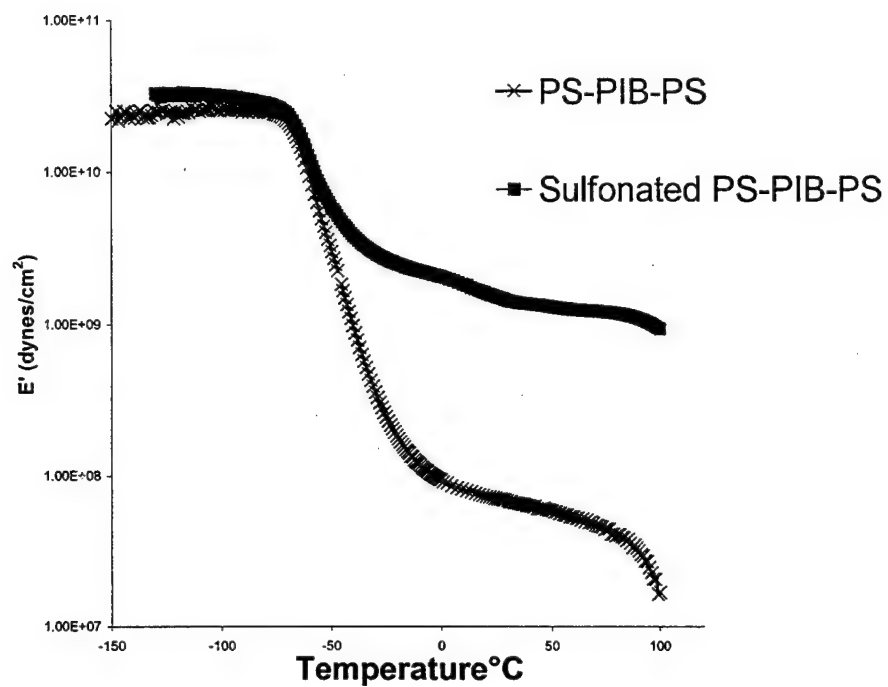
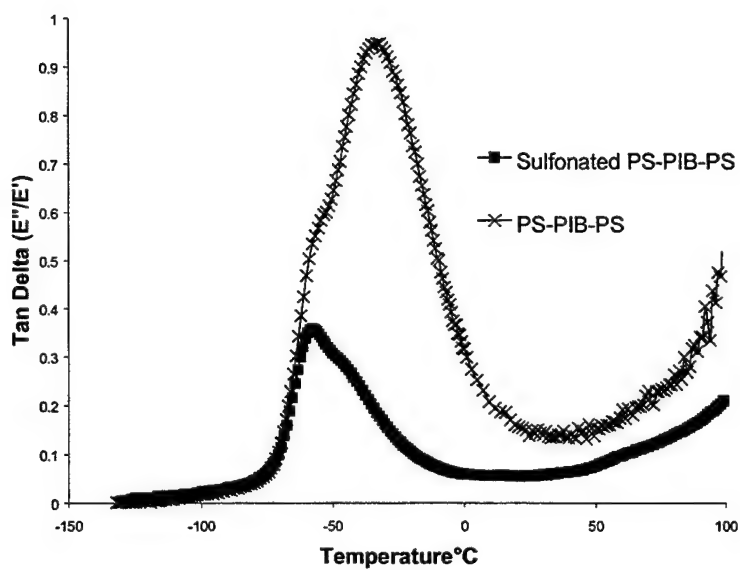**Figure 5. E' of PS-PIB-PS Copolymer and Ionomer.**

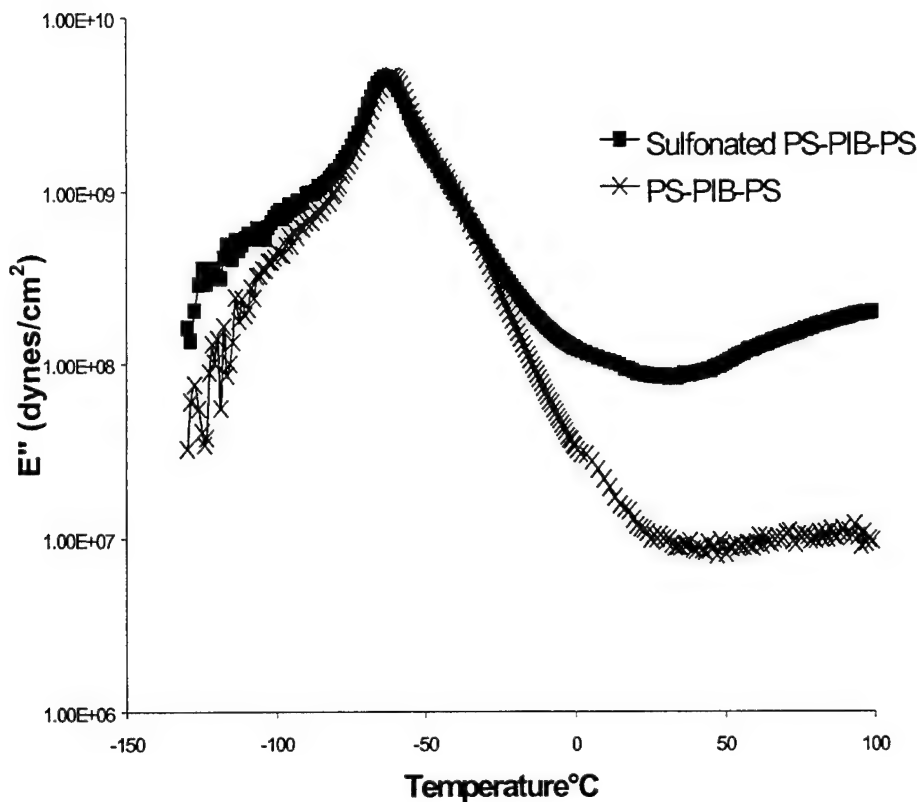**Figure 6. Tan δ of Unmodified PS-PIB-PS and Ionomer.**

7

Figure 7. E" of Unmodified PS-PIB-PS and Ionomer.

thermally stable with no indication of changes in E' at 100 °C as was observed for the nonmodified copolymer. Figure 6 shows tan δ for the two polymers. The sulfonated PS-PIB-PS exhibits a greatly reduced tan δ magnitude. Tan δ maxima for the sulfonated polymer appears to correlate with the low-temperature shoulder of the PS-PIB-PS tan δ peak. The shape of the tan δ curve for the PS-PIB-PS ionomer appears to be reversed from the unmodified copolymer. That is, rather than the presence of the low-temperature shoulder preceding the tan δ maxima as observed for PS-PIB-PS, the sulfonated polymer exhibits the prominent tan δ transition at approximately −57 °C, corresponding with the low temperature shoulder of the unmodified copolymer, followed by a higher temperature shoulder at approximately −45 °C. Similar results have been recently reported for copolymer ionomers prepared by sulfonation of the PS blocks of PS-poly(ethylene-alt-propylene) (PEP) [10]. The authors concluded that the enhancement of the high-temperature modulus is the result of association and hydrogen bonding of the sulfonic acid

groups [10]. The loss modulus of the two polymers is shown in Figure 7. These data indicate that sulfonation of the block copolymer does not affect the T_g or the magnitude of the glass transition (E" maxima). E" of the sulfonated polymer is significantly higher than the unmodified polymer at temperatures above 0 °C.

3.2 Sorption Studies. Solvent sorption and permeation studies were conducted to ascertain the effect of morphology and sulfonation of PS-PIB-PS on the ability of the polymer to absorb and transport water. Details of experimental methods used to measure permeation and calculation of diffusion coefficients are discussed elsewhere [11, 12]. Average solubility and diffusion coefficients are shown in Table 1. The hydrophobic nature of PS-PIB-PS is reflected in the solubility measurements. The unmodified copolymer exhibited a low value of water sorption, and no transport of water vapor through the film was detected. Sulfonation of approximately 20% of the styrene monomers resulted in a threefold increase in average water solubility.

Table 1. Sorption and Permeation of PS-PIB-PS and Ionomer

Polymer/Evaporation Rate	Average Solubility (S) (grams of water/ grams of sample)	Diffusion Coefficient (D) (cm^2/s)	Permeability (P) $\left(\dfrac{cm^2 \times grams\ of\ water}{grams\ of\ samples\ \times s} \right)$
PS-PIB-PS/fast	0.0547	too small to measure	too small to measure
Ionomer/fast	0.1336	3.5024×10^{-7}	4.6793×10^{-8}
Ionomer/inter	0.1636	8.7838×10^{-8}	1.4371×10^{-8}
Ionomer/slow	0.1211	1.1491×10^{-7}	1.3916×10^{-8}

3.3 Transport Studies. Transport experiments were conducted using water, acetonitrile, and a series of alcohols as individual penetrants. Acetonitrile was selected as a penetrant because its chemical structure loosely resembles the chemical agent cyanogen chloride, it exhibits moderate hydrogen bonding characteristics, and it has a very distinguishing feature in

9

the IR spectra. Figure 8 shows the kinetic plot of the IR intensity over time for water and acetonitrile. Both diffusion curves show the expected S shape and appear to be Fickian in nature. The data clearly show that water transports through the film faster than the acetonitrile. The sulfonated block copolymer membrane exhibits a breakthrough time of around 100 min for the acetonitrile penetrant. This breakthrough value surpasses the current military quality-assurance specification requirement for acceptance testing of chemical/biological protective gloves. Water molecules transport through the 8-mil membrane in approximately 25 min. The data show that the sulfonated PS-PIB-PS triblock copolymer exhibits superior semipermeable properties for chemical protective clothing compared to the currently used butyl rubber.

Figure 9 shows the kinetic IR absorbance data for several alcohols with varying aliphatic content. A clear trend becomes apparent as smaller size molecules have higher transport rates. Methanol, the smallest alcohol, diffuses very quickly through the membrane, while butanol shows no transport at all over the time scale of the experiment (450 min). The perm-selective properties of the sulfonated triblock copolymer membrane is demonstrated by its size selectivity characteristics with respect to penetrant. Increasing the aliphatic content of the alcohols by only three CH_2 groups results in a significant decrease in transport rate.

3.4 Characterization of Microstructure. The morphology in both modified and unmodified PS-PIB-PS triblocks was studied using a combination of SAXS and TEM. TEM results, shown in Figures 10 and 11, reveal a microphase-separated morphology in both the unmodified and sulfonated PS-PIB-PS triblocks. In the unmodified copolymers, the morphology is typical of self-assembled cylindrical systems and displays considerable long-range order (Figure 10). The SAXS curves for these materials, shown in Figure 12, show evidence of long-range order as well. Scattering peaks occur at positions that are multiples of $\sqrt{3}$, 2, $\sqrt{7}$, and 3× the position of the primary reflection, indicating that the copolymer forms a hexagonally packed cylindrical morphology. The degree of long-range order depends somewhat on the processing technique, increasing as the time for film casting increases, as evidenced by sharper
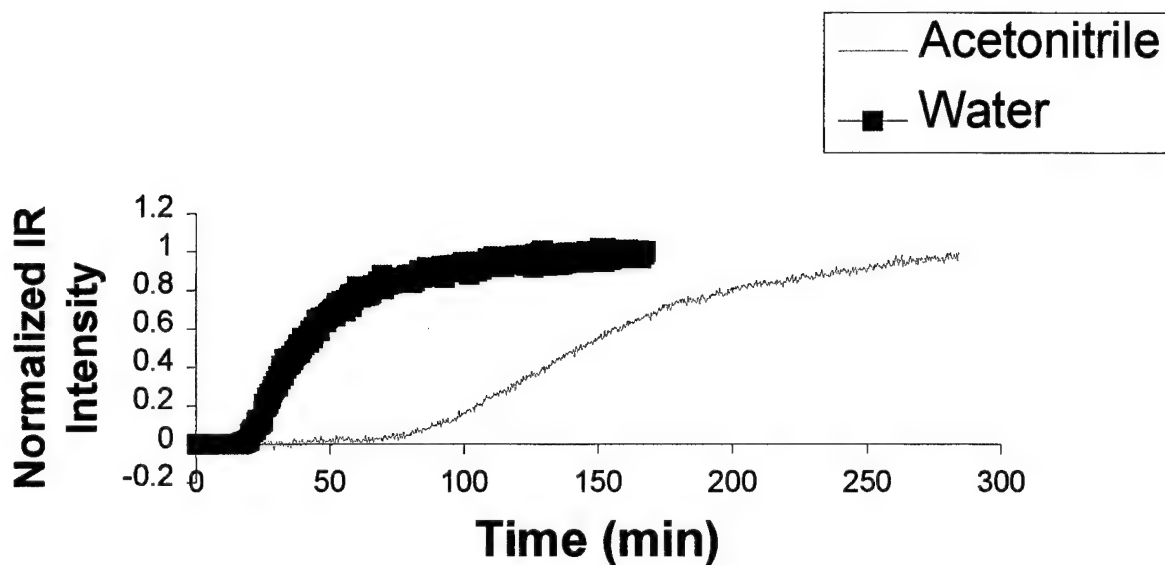
10

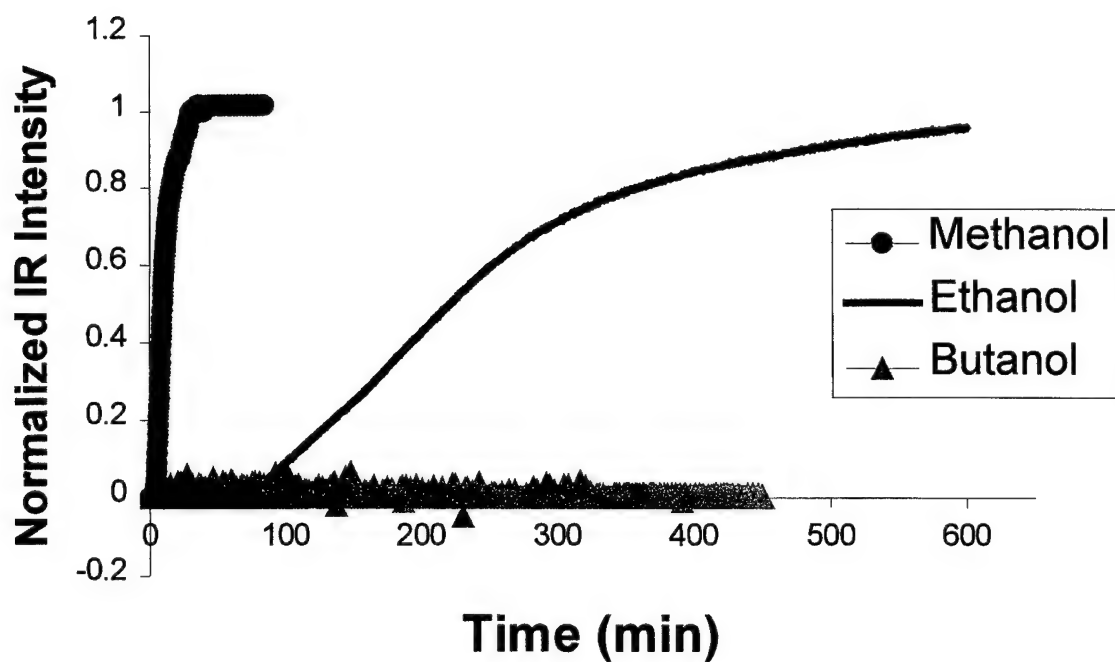**Figure 8. Diffusion of Acetonitrile and Water Through Sulfonated PS-PIB-PS Triblock Copolymer.**

Figure 9. Diffusion Curves for Various Alcohols Through Sulfonated Block Copolymer.
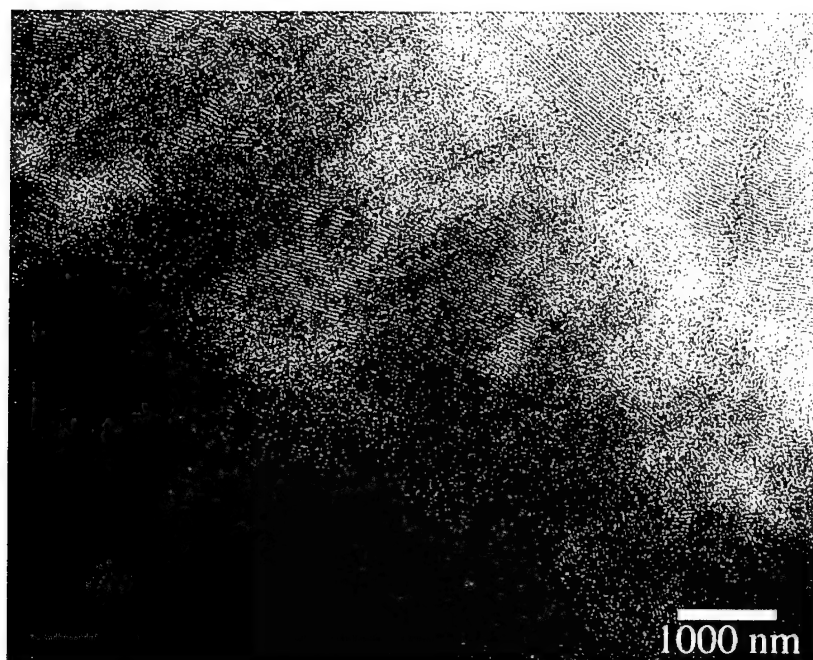
11

Figure 10. Unmodified PS-PIB-PS Film Formed Under Fast Evaporation Conditions. PS Phase Was Stained by RuO_4 and Appears as the Dark Regions.
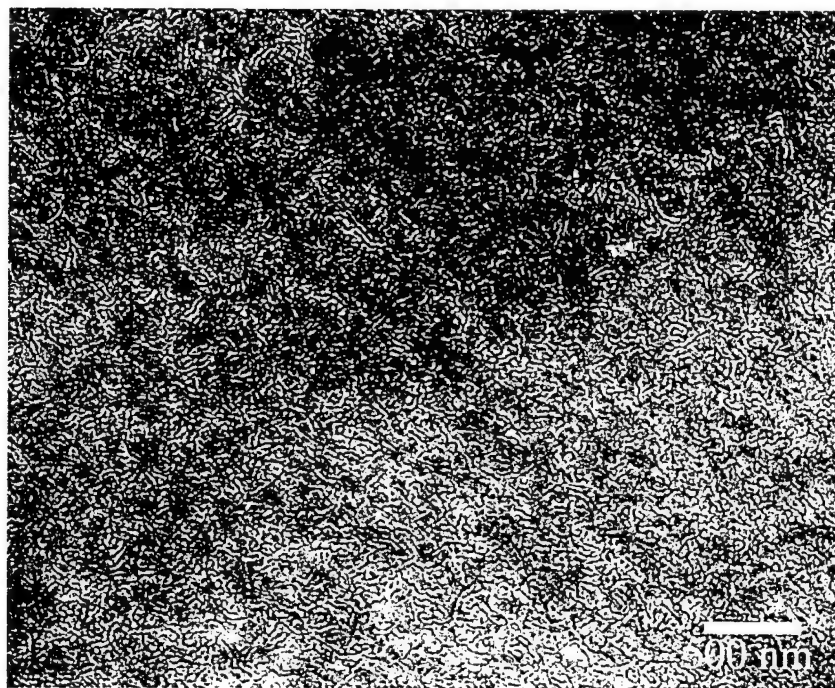

Figure 11. Sulfonated PS-PIB-PS Film Formed Under Fast Evaporation Conditions. PS Phase Was Stained by RuO_4 and Appears as the Dark Regions.
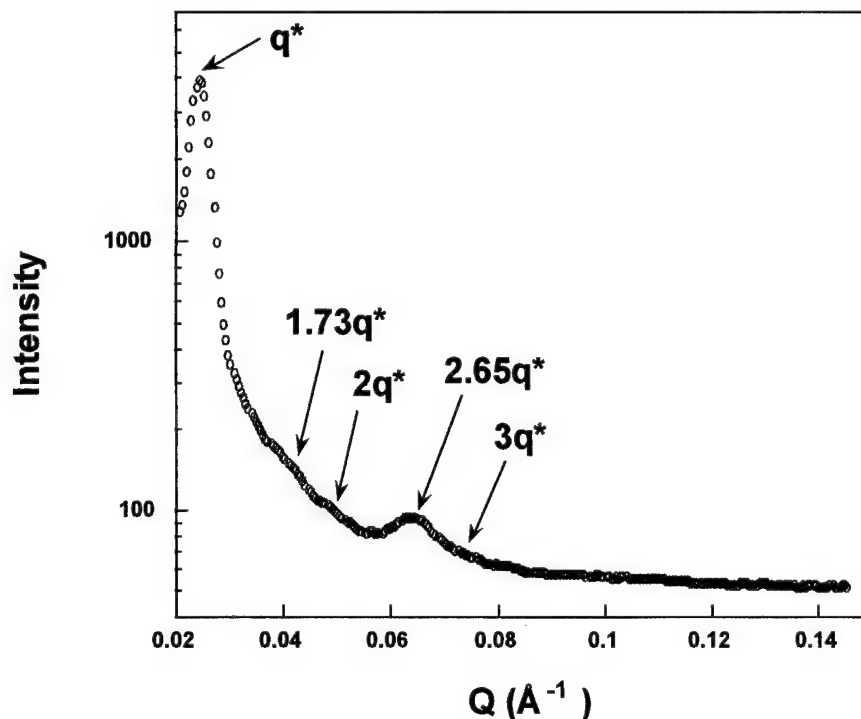
12

Figure 12. SAXS Intensity vs. Scattering Vector, Q, for PS-PIB-PS Triblock, Slow Casting Condition. Peaks Occur in the Sequence 1, $\sqrt{3}$, 2, $\sqrt{7}$, 3 Times the Position of the Primary Scattering Peak, q*. The Primary Scattering Peak Occurs at q*= 0.0245 Å.

scattering peaks and more prevalent high-order reflections (Figure 13). The most significant change to the morphology occurs as a result of sulfonating the PS block. After sulfonation, the long-range order of the copolymer is severely disrupted. The electron micrograph, Figure 11, shows that the sulfonated triblock forms cylinders that order only locally. The SAXS data also show a loss of long-range order, as evidenced by the broadening of the scattering peaks, and the lack of clearly defined scattering peaks at higher Q values (Figure 14). The disruption of long-range order upon sulfonation is similar to effects observed in other triblock thermoplastic elastomer systems and has been previously reported [1, 13].
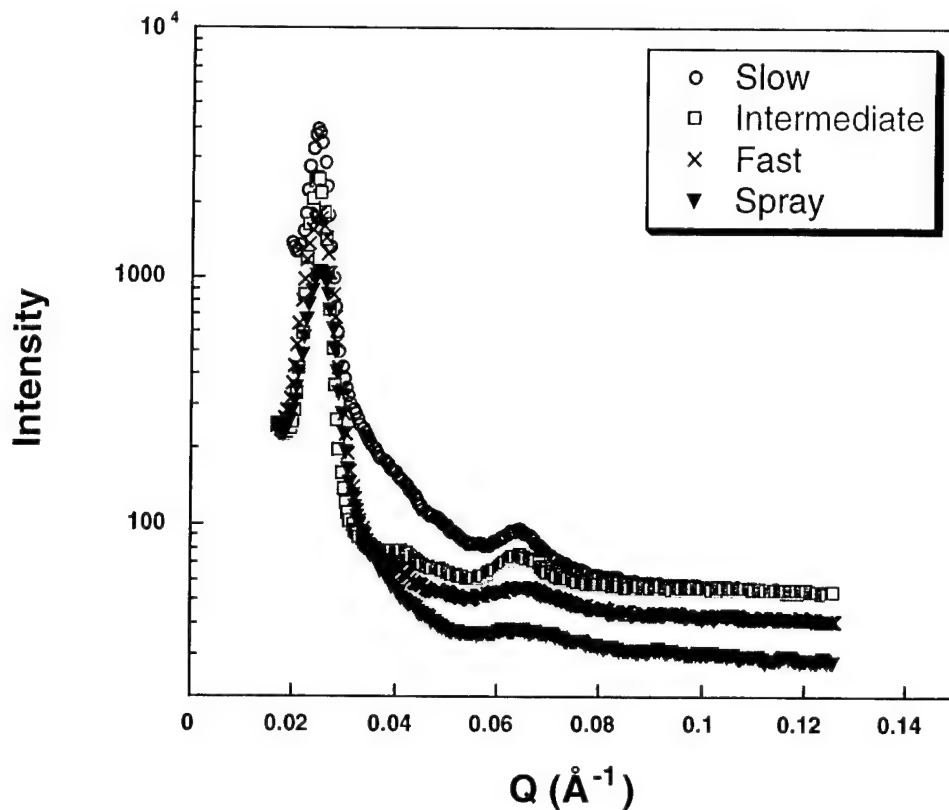
Figure 13. SAXS Intensity vs. Scattering Vector, Q, for PS-PIB-PS Triblocks at Different Casting Conditions. For All Conditions, the Primary Scattering Peak Occurs at q*= 0.0245 Å.

4. Conclusions

The morphology and viscoelastic properties of PS-PIB-PS triblock copolymers were studied with respect to film processing and sulfonation of approximately 20% of the styrene monomers. TEM and SAXS studies confirmed that the copolymers exhibit phase-segregated cylindrical domain morphology and indicated that slow evaporation rates enhanced long-range order of the PS domains, while sulfonation greatly perturbed the morphology. Sulfonation of the styrene blocks had a dramatic effect on dynamic mechanical properties. Ionomers of PS-PIB-PS exhibited a greatly increased rubbery plateau E' and a dramatic reduction in tan δ magnitude. These observations are believed to be related to associations of the sulfonic-acid groups that
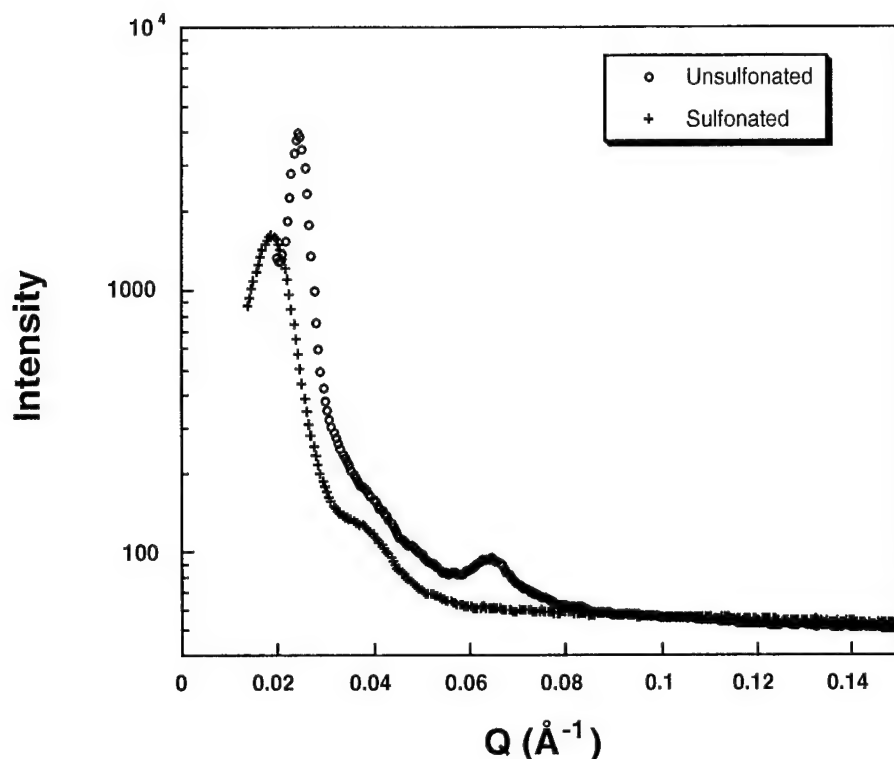
Figure 14. SAXS Intensity vs. Scattering Vector, Q, for Sulfonated and Unsulfonated PS-PIB-PS Triblocks, Slow Casting Conditions. The Primary Scattering Vector in the Sulfonated System, q^*_s, Occurs at a Lower Value Than for the Unsulfonated System Due to Volume Expansion in the PS Block.

inhibit slippage of the amorphous chains. Sorption and transport studies showed that the ionomer exhibited significantly improved water-transport properties and exhibit selectivity between small organic molecules. Collectively, the mechanical properties and ease of processing the sulfonated PS-PIB-PS triblock copolymer films, combined with their ability to transport water and block organic molecules, render these membranes applicable for chemical protective clothing for military applications. The unique properties of these polymers would also be useful for nonmilitary applications including protective clothing for "first responders" in chemical-threat situations or for hazardous materials handling. Future studies are planned to specifically address the morphological features in the ionomers with respect to sulfonation levels and counterion substitution.

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DMA, triblock copolymer, ionomer, sulfonation, microstructure, morphology, solvent transport

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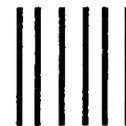**(DO NOT STAPLE)**

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